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CATALYSIS OF NITRAMINE PROPELLANTS BY
METAL BOROHYDRIDES

Robert A. Fifer
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I. INTRODUCTION

For a couple of decades now, there has been an ongoing search for effective catalysts for nitramine propellants. At the present time, there are active research or test programs at several installations devoted to the search for nitramine propellant catalysts. Despite all of this activity, no effective catalysts have been found. A few additives have been found to increase the burning rate of HMX or RDX propellants under some conditions, but generally these results correspond to one of three situations: (a) burning at very low pressures (a few MPa or less) where the binder, or nitramine-binder interaction, controls the rate, (b) formulations containing relatively large concentrations (e.g., 10-50%) of a "co-oxidizer" like ammonium perchlorate (AP) or triaminoguanidine nitrate (TAGN), which increase the burning rate primarily by virtue of the high burning rate of the "co-oxidizer", and (c) formulations containing an energetic (nitrocellulose [NC] based) binder plus additives (generally lead compounds with graphite) that are known to accelerate the burning rate of NC. No additives have been reported that enhance the burning rate of inert-binder nitramine propellants at high pressures, or which give propellant burning rates higher than that for the neat nitramine.

In 1979, Fifer and Cole¹ reported that 10 or 20% lithium borohydride (LiBH_4) increased the impetus bomb pressurization rate for granular (150-300 μm) HMX by more than an order of magnitude. An analysis of the pressure traces indicated that pressurization rates like those observed could only occur if the borohydride resulted in a substantial increase in the HMX burning rate over the pressure range of the experiments (0-180 MPa). The enhanced pressurization with LiBH_4 was reproducible. The effect diminished with increased HMX particle size (the burning of 1600 μm HMX particles was not appreciably "catalyzed" by LiBH_4), or if the two powders were not thoroughly mixed before ignition. More recently, a few impetus bomb tests have been carried out with sodium borohydride (NaBH_4). In a couple of runs, rapid pressurization was observed, as with LiBH_4 . In other runs, the effect was negligible. The causes of this variability were not investigated.

Realizing the potential significance of the impetus bomb results, an attempt was made to prepare a few propellant samples for regression rate measurements in a constant pressure chamber ("strand burner"). Lacking in-house propellant fabrication facilities, a simple mixing and pressing procedure was employed, using "class E" (<44 μm) HMX, and as received (>50 μm) cellulose diacetate (CA) and LiBH_4 (or NaBH_4). The ingredients were handled in a dry box (after an explosion occurred while attempting to press a HMX/CA/ LiBH_4 mixture that had picked up some moisture), mixed briefly in a "wiggle-bug" shaker normally used to prepare KBr pellets, and pressed at about 480 MPa (70,000 psi) into ~92% TMD parallelepipeds with dimensions 22.5 x 4.7 x ~3.5 mm. These samples were equipped with fuse wires, inhibited with grease, and burned at 41.4 MPa (6,000 psi), with the following results:

¹R.A. Fifer and J.E. Cole, "High Force-Low Product Molecular Weight Propellants for Gun Applications," 16th JANNAF Combustion Meeting, CPIA Publication No. 308, Vol. I, pp. 385-389, December 1979.

TABLE 1. BURN RATES FOR PRESSED STRANDS

<u>Propellant</u>	<u>Rate, mm/s at 41.4 MPa</u>
75% HMX + 25% CA	85
75% (HMX + 10% LiBH ₄) + 25% CA	700
70% HMX + 30% CA	46
70% (HMX + 10% LiBH ₄) + 30% CA	330
70% (HMX + 10% NaBH ₄) + 30% CA	110

Apparently, substituting 6.4-6.8% LiBH₄ for HMX gave a seven- to eight-fold increase in rate, while 6.4% NaBH₄ increased the rate by more than a factor of two. Part of the difference in apparent effectiveness of the two salts is undoubtedly the fact that a given weight of LiBH₄ (M.W.=21.79) has 73.7% more BH₄ than NaBH₄ (M.W.=37.84). The burning in these tests was not uniform, however, so the rates shown are only approximate. The erratic burning was thought to be due either to inadequate mixing or to possible convective burning effects. If convective burning (in-depth burning in porous samples) had been induced by the borohydrides, the increases in regression rate would not correspond to real increases in the laminar (conductive) burning rate, and would only be "apparent" burning rate effects. Therefore these results, though encouraging, were not considered to be conclusive. A conclusive test would have to involve "professionally" fabricated propellants made by a process other than cold pressing.

II. PROPELLANT FORMULATION

Arrangements were made for the Naval Ordnance Station, Indian Head, MD (NOSIH) to fabricate a control and catalyzed propellant in unperforated strand configuration for these tests. NaBH₄ was chosen as the "catalyst" since it is much easier to work with than LiBH₄. LiBH₄ must be handled in a totally moisture-free atmosphere. It is very hygroscopic, and in air quickly becomes wet and immediately begins decomposing with evolution of gas and generation of heat. If placed on a combustible surface (e.g., paper) in air, a fire is likely to result after a short time. On the other hand, NaBH₄, though hygroscopic, often can be handled for short periods of time in low humidity air. A dihydrate forms upon exposure to moisture, but this dihydrate is fairly stable (except for long term storage), and will regenerate the anhydrous borohydride if heated above the 36°C transition temperature. If kept above this temperature, no hydration or decomposition occurs in air. NaBH₄ is stable in air up to 300°C, and in a vacuum or inert gas to 400°C or higher. References 2 and 3 summarize the properties of the borohydrides.

²R.M. Adams and A.R. Siedle, "The Hydroboron Ions (Ionic Boron Hydrides)," *Boron, Metallo-Boron Compounds and Boranes*, R.M. Adams, ed., Chapter 6, pp. 385-396, 398-409, 424-430, 1964.

³B.D. James and M.G.H. Wallbridge, "Metal Tetrahydroborates," *Progress in Organic Chemistry*, S.J. Lippard, ed., Vol. II, pp. 127-136 and 141-144, 1970.

Since it was not known whether NaBH_4 would be compatible with a curing binder, it was decided to prepare the propellants using a thermoplastic binder and a melt-extrusion procedure. A Kraton G1652 binder with Tufflo 6056 plasticizer were chosen since NOSIH was already familiar with their use for nitramine propellants. Kraton G1652 is a styrene-ethylene/butylene-styrene (S-EB-S) rubber copolymer (Shell Chemical Co.), and Tufflo 6056 is a hydrocarbon type plasticizer. Since these two materials contain no oxygen, their use results in a very cool, underoxidized propellant. In order to minimize the possibility of any porosity in the finished propellants, a relatively low solids loading (70% HMX or HMX/NaBH_4) was selected, although we since have learned that a 75 or 80% solids loading could probably have been used with little increased risk of porosity.

The control and "catalyzed" propellants were made with the following compositions (in weight percent):

TABLE 2. PROPELLANT COMPOSITIONS

<u>Formulation</u>	<u>HMX</u> %	<u>KRATON G1652</u> %	<u>TUFFLO 6056</u> %	<u>NaBH_4</u> %
Control	70	15	15	0
Catalyzed	63.6	15	15	6.4

The mean particle size of the "ground" HMX was about 7 μm , while that of the NaBH_4 (Callery Chemical Co., 98% min.) was 60 μm .

The processing of these propellants, as carried out by NOSIH, was as follows: The ground HMX was hand slurried in hexane ("catalyzed" propellant) or ethanol (control propellant), and then mixed in a one-half pint horizontal mixer for 10 minutes at 49°C (120°F). For the "catalyzed" propellant, dried NaBH_4 , hand slurried in toluene, was added and mixing continued for an additional 10 minutes at 49°C. The Tufflo plasticizer was then added to the mixer, followed by yet another 10 minutes of mixing at 49°C. The lid of the mixer was then removed, and with the mixer still running at 49°C, the mixture was dried to a powdery or flakey consistency (~20 minutes) under a stream of air. It was then removed from the mixer and dried overnight at 60°C. Several such 60 g mixes were prepared and blended together to obtain the required sample size. Finally, the powder was preheated to 82°C for 30 minutes, and then extruded through a 7.62 mm (0.300 in.) die using a 82°C press temperature, 1.38 MPa (200 psi) powder pressure, and 7 cm/min. ram rate.

It was reported by NOSIH that on cooling, water condensed on the surface of the "catalyzed" propellant. When delivered, this propellant was dry, but the surface had a more powdery texture than for the control propellant due to the water condensation and reactions at the surface. Tests were performed in which thin layers (e.g., 100-200 μm) were shaved off the surface of the propellant. Small droplets appeared in a few minutes just like for deeper

cuts, suggesting that the NaBH_4 had reacted only at the surface of the propellant. Both propellants were very flexible; the "catalyzed" propellant was a little less flexible, however, and broke more easily if bent severely.

Densities of the two propellants were as follows:

TABLE 3. PROPELLANT DENSITIES

	<u>Control</u>	<u>Catalyzed</u>
Theoretical Density*	1.414	1.364
By Weight and Dimensions	1.411 + .004	1.351 + .005
By Helium Pycnometer	1.418 + .002	1.363 + .002

 *Based on $\text{HMX}=1.90$, $\text{Kraton}=0.910$, $\text{Tufflo}=0.863$, $\text{NaBH}_4=1.074$

Since the densities determined by weight and dimensions are a little lower than those determined by gas displacement, there may be a very small amount of porosity in the "catalyzed" propellant. If so, it might exist only at the reacted surface rather than throughout the bulk of the propellant. The propellants had no measurable permeability, so convective burning effects would not be expected.

Constant volume thermochemical calculations were carried out for the two propellants using the NASA-Lewis thermochemical code. For a 0.1 g/cc loading density, the results are:

TABLE 4. THERMOCHEMICAL CALCULATIONS

	<u>Control</u>	<u>Catalyzed</u>
T_f , K	1863	1866
M^*	19.288	20.062
I, J/g	803	773
Products, mole%		
H_2	32.4	34.3
CO	28.0	20.1
C(s)	16.1	20.9
N_2	15.1	13.4
CH_4	5.8	6.5
H_2O	1.8	1.4
$\text{NaBO}_2(\text{g})$	----	2.6
CO_2	0.4	0.2
HCN	0.2	0.2
NH_3	0.2	0.2

 *total mass/moles of gas only.

Based on the following heats of formation (Kcal/mole): HMX , 17.9; NaBH_4 , -45.65; Kraton G1652 , -2.02 (formula $\text{C}_{7.3}\text{H}_{12.1}$); Tufflo 6056 , -3.321 (formula $\text{C}_{7.3}\text{H}_{13}$).

It can be seen that the sodium and boron in the "catalyzed" propellant are not predicted to form condensed products at equilibrium, but the control and "catalyzed" propellants are predicted to produce roughly 16 and 21 mole percent solid carbon, respectively. The high yield of carbonaceous residue from these propellants made the burning rate measurements difficult, as described below.

III. PROPELLANT DESCRIPTION

The propellants consisted of strands one to two meters in length and 8.1 mm in diameter. For the tests, samples 40 mm long were cut. The end to be ignited was shaved to provide a tab for the ignition wire to perforate.

The strands were rubbery with a consistency of Tygon tubing of similar diameter. Shaving with a razor blade was the major shaping technique. The material was somewhat easier to cut than Tygon.

IV. MEASUREMENT TECHNIQUES

Burn rates were determined in two high pressure chamber systems. A windowed chamber was used to obtain data up to about 100 MPa. This chamber provides a window opening of 12 mm by 36 mm. A video tape system was used to record the burn event. A metric grid was placed near the sample for distance calibration. The TV camera was adjusted to provide approximately a five to one magnification on the monitor. The time resolution was limited to the 60 Hz recording rate of the TV system. Backlighting and sample luminosity were used to determine the position of the burn surface.

A closed chamber with standard fuse wire techniques was used for pressures up to 300 MPa. Fuse wire data was recorded on both a digital oscilloscope and a digital electronic timer.

V. SURFACE INHIBITION

It is normally necessary to inhibit the sides of the propellant strand to prevent the spread of the flame along the sides of the sample. In order to obtain the correct burning rate, it is necessary that combustion occur in a single plane normal to the axis of the propellant. Normal procedure for gun propellant testing is to coat the sides of the propellant sample with a thin layer of tar/asphaltum. The tar is dissolved in a volatile solvent and commonly applied to the strand by dipping the sample into the solution and allowing the solvent to evaporate. The tar provides a thin, adherent film that does not burn readily. Caution is required to be sure that the solvent is totally evaporated from the sample, including the propellant. The dried tar layer provides a good vapor barrier for any solvent that has migrated into the propellant.

As mentioned above, thermochemical calculations show that these propellants should produce a large amount of solid carbon. Under the best of conditions, this would result in a very smoky flame. In these tests, the formulations were relatively cool burning. This resulted in the free carbon

forming a weak sponge above the burning surface. In the pressure range of 10 MPa to 50 MPa, the sponge was disrupted during the burn. As the pressure neared 100 MPa, the sponge became progressively denser; after a test, the coherent sponge would be recovered as long cylindrical pieces of about the original sample diameter. The material burned like the old fireworks device known as a "Snake," with the carbon sponge being extruded from the burning surface. The low luminosity associated with the low flame temperature and the opacity of the carbon sponge made observation of the burn front difficult.

Problems were encountered with viewing the burn zone through the tar coat. Several thicknesses were tried. Asphalt/tar was dissolved in chloroform at various dilutions in order to provide different thicknesses of film when the sample was dipped into the solution. At thicknesses which produced a visually black coating, it was not possible to detect the burn front with the video system. At thicknesses which corresponded to a brown tar coat, erratic burn data was obtained. This may have been due to difficulty in properly locating the burn surface or due to the chloroform solvent migrating into the propellant and not being properly removed. Another method was sought that would allow recording with the video system.

A clear epoxy coating was tried on the control and catalyzed samples. The epoxy coating was observed to peel from the sample during a burn. The flame would flash down the side of the sample between the peeled epoxy and the propellant. The epoxy was definitely less adherent to the catalyzed material. Some of the tests appeared to give a proper inhibition but the data were not reliable.

A coating of grease was the next inhibitor tested. Kel-F, a fluorocarbon grease, was smeared on the sides of the samples. Difficulties were experienced in obtaining a uniform thickness of the grease. On some of the samples, there appeared to be a flashing (ignition) down the sides of the propellant. Whether this was due to the grease melting and running down the sides of the sample or to ignition through thin patches was not determined. The vapors from the greased samples appeared to corrode the chamber walls and testing was discontinued.

Tests were conducted with the propellant immersed in a clear oil. The very top of the propellant was left above the oil to provide an ignition site. The oil was contained in a flat-sided vessel of clear acrylic. With the faster burning catalyzed propellant at higher pressures, the burn appeared to be good and was readily detectable. The gas evolution rate was high enough to keep the oil away from the burn surface.

At lower pressures, and especially with the slower control samples, it appeared that the burning surface was highly concave. Some samples were recovered from low pressure runs in which the burn had extinguished. Deep (one diameter) cavities were found on the burn surface. Whether the walls of the cavity had been cooled by the oil or the oil had diffused into the surface layer of the sample was not determined. The oil that was used for most of these tests was vacuum pump oil (Hyvac brand).

Upon reexamination of the higher pressure runs with oil immersion it was decided that there was no way of determining the burn surface shape (concave or convex).

It was decided to gel the oil to reduce the motion of the oil and thus possibly reduce the convective heat transfer. Upon gelling the oil with a modified clay agent, it became apparent that the gelled oil was not clear enough for photographic purposes. Also it was found that the viscosity of the gelled oil could be adjusted to produce a relatively uniform dip coat on the samples. A gel-coating technique was therefore selected for the final set of experiments. The dip coat used was approximately one millimeter thick and relatively clear. A special holder was used to protect the gel layer during chamber assembly. The results appeared to be quite good and consistent. Although clouded by the propellant combustion, the gelled oil layer remained in position after the burn, keeping very nearly its original diameter.

The gelling agent used to make the oil gel coat was Bentone 38, a sample of which was donated by NL Industries, Inc. of Hightstown, New Jersey. This material is a modified montmorillonite clay that is used as a rheological additive for nonpolar and intermediate polarity organic liquids. A low vapor pressure oil was desired as the base for the gel coat. A vacuum pump oil (Hyvac brand) was readily available and appeared to be a good material for these tests. Two tablespoons of the dry Bentone 38 were stirred into 300 ml of the oil. A whisk was used to break up the clumps. An ultrasonic probe was used to disperse the clay. Five minutes of dispersion gave a visibly uniform mixture. The Bentone 38 requires a polar activator to form a gel. Thirty milliliters of acetone was added while stirring; final dispersion with the ultrasonic probe required an additional five minutes. The acetone allows the clay platelets to separate and form the gel matrix.

The gelled oil became stiffer over a period of several days. To lower the viscosity, additional oil was added and the ultrasonic probe was used to ensure dispersion.

Air that was entrained in the clay powder during the initial mixing caused numerous small bubbles to remain in the liquid through the stages of gellation. Subjecting the mixture to a vacuum before adding the activator would have allowed the bubbles to escape and would have resulted in a clearer gel coat.

A number of advantages of using the gel coat are to be noted. The base liquid may be chosen to be compatible with the propellant material. The gel coat may be applied within minutes of use in the chamber rather than requiring a lengthy curing period or solvent drying period. The clarity of the coating allows good determination of the position of the burn surface. The finite strength (low) of the gel matrix allows a fairly thick coating to be applied. The liquid may be selected to wet the propellant sample to prevent peeling of the coating during the burn cycle. In these tests, the gel coating did not melt and run down the sides of the sample as the grease and the tar coatings did. If a thinner coating is desired, the gel may be easily thinned by addition of more liquid.

VI. BURN RATE TESTS

Extensive testing was done to obtain a good inhibitor for use with the windowed chamber tests, as described above. The basic problem was due to the low luminosity of the burn front and to the dense smoke in the burn

products. In the closed chamber tests with fuse wire detection, the combustion products also caused problems. The carbon sponge was electrically continuous (150 ohm/cm). This caused a shorting of the ignition circuit to the fuse wire circuits, and also produced a continuity path for a single fuse wire circuit when the fuse wire melted. Attempts were made to spring load the fuse wires so that they would pull free of the carbon sponge upon melting. This was only partially successful. The melted fuse wire was still frequently able to maintain contact with the sponge of carbon, producing noisy, unreliable break signals. Triggering of the timer and the digital oscilloscope was therefore not reliable at high pressures. The shorting of the ignition wire to the fuse wire circuits caused a large 60 Hz signal to appear in the fuse wire circuits, generally near the time of burn-through.

The data from the oil gel coat tests for the catalyzed and control propellant samples are shown in Figure 1. The straight lines were generated from least squares fits of the log R vs. log P data. Only data for burn rates above 4 mm/s were used in generating these lines as the lower rate data visibly deviated from the higher pressure line. Table 5 lists the data used in Figure 1 for the control propellant samples.

TABLE 5. BURN RATE DATA, CONTROL SAMPLES, OIL GEL COAT

<u>PRESSURE, P</u> <u>MPa</u>	<u>RATE, R</u> <u>mm/s</u>
12.9	2.32
18.4	3.12
30.4	3.85
36.8	4.27
58.5	7.75
67.6	9.52
101.5	15.6
114.	19.0
194.	35

The data faster than 4 mm/s were least squares fitted to the equation:
 $R = aP^n$. This yields

$$R = 0.04407 P^{1.272} \quad (1)$$

where R is in mm/s and P is MPa.

The data for the "catalyzed" propellant is given in Table 6.

The rate data above 4 mm/s were least squares fitted to the equation:

$$R = 0.1635 P^{1.172} \quad (2)$$

where R is in mm/s and P is in MPa. The pressure exponent of the "catalyzed" propellant is apparently a little lower than that of the control propellant, suggesting that the NaBH_4 (or its decomposition products) exerts its influence in the condensed phase or at the surface, but not in the flame zone.

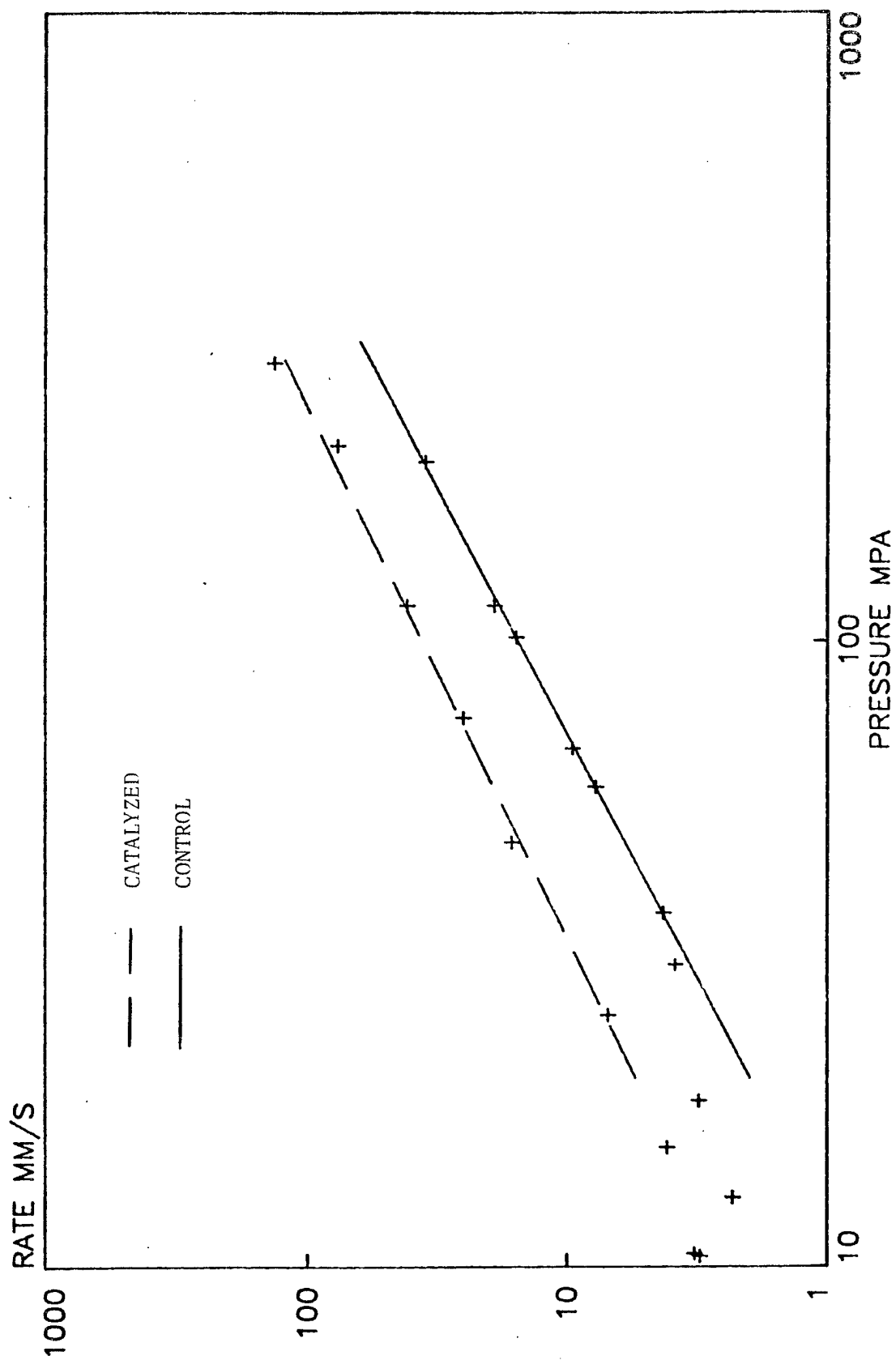


FIGURE 1. BURN RATE, CONTROL AND CATALYZED PROPELLANTS, STRAND BURNER RESULTS

TABLE 6. BURN RATE DATA, CATALYZED SAMPLES, OIL GEL COAT

<u>PRESSURE, P</u> <u>MPa</u>	<u>RATE, R</u> <u>mm/s</u>
10.4	3.10
10.5	3.25
15.5	4.13
25.2	6.94
47.7	16.3
75.5	25
114	41.1
206	75.8
278	133

Table 7 compares the burn rates predicted by Equations 1 and 2 at selected pressures.

TABLE 7. CALCULATED RATES AT SELECTED PRESSURES

<u>PRESSURE, P</u> <u>MPa</u>	<u>RATE, CONTROL</u> <u>mm/s, Eqn. 1</u>	<u>RATE, CATALYZED</u> <u>mm/s, Eqn. 2</u>	<u>RATIO</u>
10	0.824	2.42	
20	1.99	5.47	
50	6.39	16.0	2.50
100	15.4	36.1	2.34
200	37.2	81.3	2.19
300	62.4	131	2.10

The calculated values below 4 mm/s do not match the experimental values and are included for comparison purposes. Experimentally, the burning rate curve for the control propellant levels off with decreasing pressure, so that at 10 MPa the catalyzed propellant only burns about 50% faster than the control propellant.

The minimum pressure at which stable burning could be achieved was not determined in this sequence of tests. The control propellant would ignite and then extinguish at 10 MPa. The catalyzed propellant would burn at 5 MPa.

VII. CLOSED BOMB DATA

Samples of control and catalyzed propellant were cut into 6.6 mm lengths by rolling lengths of the propellant across a multiblade cutting device fabricated from razor blades and spacers. Blake thermochemical code calculations were also carried out to obtain estimates of covolume and other parameters needed for closed bomb data reduction. The samples and thermochemical calculations were submitted to the BRL closed bomb team for

analysis. Four experiments were carried out, as detailed in Appendix A. Pressurization was rather slow due to the low burning rate and surface area of the unperforated grains, and the maximum pressure only reached 82-85% of that predicted theoretically, presumably due mainly to heat loss effects. The derived burning rate plots were fairly linear from 41 MPa (6 Kpsi) to roughly the 80% burn point (~230-250 MPa). The resulting burning rate laws can be averaged for each propellant to give $R = 0.09856 P^{1.044}$ mm/s for the control propellant and $R = 0.1843 P^{0.967}$ mm/s for the NaBH_4 catalyzed propellant. The comparison of strand burner and closed bomb results is shown in Table 8.

TABLE 8. COMPARISON OF STRAND BURNER AND CLOSED BOMB BURNING RATES

<u>P, MPa</u>	<u>Rate, Control, mm/s</u>		<u>Rate, Catalyzed, mm/s</u>	
	<u>Strand Burner</u>	<u>Closed Bomb</u>	<u>Strand Burner</u>	<u>Closed Bomb</u>
10	0.824	1.09*	2.42	1.71*
20	1.99	2.55*	5.47	3.34*
50	6.39	5.85	16.0	8.10
100	15.4	12.1	36.1	15.8
200	37.2	24.9	81.3	30.9
300	62.4	38.0	131	45.8

**extrapolated outside of range of data*

The closed bomb data does not agree well with the strand burner data. The pressure exponents are more than 0.2 units lower for the closed bomb, the high pressure burning rates are significantly lower for the closed bomb, and the closed bomb data suggests a much smaller catalytic effect, especially at the higher pressures. Possible reasons for these discrepancies are being investigated.

VIII. SUMMARY

The burn rate of an HMX propellant formulation was increased by approximately a factor of 2.2 over the 30-300 MPa pressure range by substituting 6.4% sodium borohydride for HMX.

The high level of free carbon in the combustion products of these propellants caused problems in obtaining the burn rate data and would not be characteristic of a functional propellant. An improved formulation with a higher solids loading (80% instead of 70%) is being obtained. This should produce considerably less carbon, and have a higher burning rate. Future plans call for tests with more energetic binders (i.e., having some oxygen content), to determine if sodium borohydride is equally effective in faster burning, smokeless nitramine propellants.

It is proposed that the borohydrides are effective burning rate accelerators because they--or the BH_3 products they produce on decomposition--are reducing agents. (Most previous attempts to catalyze nitramine propellants have involved tests with oxidizing agents.) Tests with other reducing agents will provide a test of this hypothesis.

APPENDIX A

CLOSED BOMB DATA FOR CONTROL AND CATALYZED PROPELLANTS

APPENDIX A

CLOSED BOMB DATA FOR CONTROL AND CATALYZED PROPELLANTS*

J. Omar Doali and Arpad A. Juhasz

Two closed bomb experiments were successfully obtained for each propellant (6.6 mm unperforated strands). The data were obtained at 16°C in a 195.3 cc bomb with a Kistler 607C transducer, using a larger than normal charge of black powder pellets to insure ignition. The experimental conditions and measured and calculated results are summarized in the accompanying table, along with the BLAKE code parameters used in the data reduction. A constant heat loss was assumed. The derived R vs. P curves showed very good agreement for the two control propellant runs. For the two catalyzed propellant runs, agreement was not quite as good. Figures A-1 and A-2 show the appearance of derived R vs. P plots for control sample #1 and catalyzed sample #1, respectively. After each experiment, a large fraction of the bomb volume was found to be packed with a black carbonaceous residue.

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TABLE A-1. DATA FOR CLOSED BOMB EXPERIMENTS

<u>Experiment</u>	<u>Control #1</u>	<u>Control #2</u>	<u>Catalyzed #1</u>	<u>Catalyzed #2</u>
weight, g	55.49	55.77	55.97	55.77
ρ , g/cc	0.2841	0.2856	0.2866	0.2855
weight B.P., g	2.45	2.68	2.68	2.68
BLAKE Code Data (No B.P.)				
T_f , °K	2034	2034	2024	2024
M	20.689	20.689	21.579	21.579
I, J/g	816.7	816.7	779.2	779.2
b, cc/g	1.232	1.232	1.182	1.182
γ	1.2495	1.2495	1.2300	1.2300
P_{max} , MPa	371.9	376.2	352.8	350.9
Measured Results				
P_{max} , MPa	315.7	313.8	289.2	291.1
t to 10% P_{max} , ms	453	452	206	204
t to 90% P_{max} , ms	564	564	294	295
t to 100% P_{max} , ms	656	659	408	414
t 10-90% P_{max} , ms	110.6	111.2	87.9	91.2
Calculated Results				
a in $R = aP^n$ mm/s	0.09724	0.09986	0.1632	0.2089
n in $R = aP^n$ mm/s	1.046	1.042	0.997	0.936
P/P_{max} range for R	0.13-0.83	0.13-0.79	0.14-0.81	0.14-0.81
P range, MPa, for R	41-262	41-248	41-235	41-234
R at 50 MPa, mm/s	5.82	5.89	8.07	8.13
R at 100 MPa, mm/s	12.0	12.1	16.1	15.6
R at 200 MPa, mm/s	24.8	25.0	32.2	29.8
R at 300 MPa, mm/s	37.9	38.1	48.2	43.5

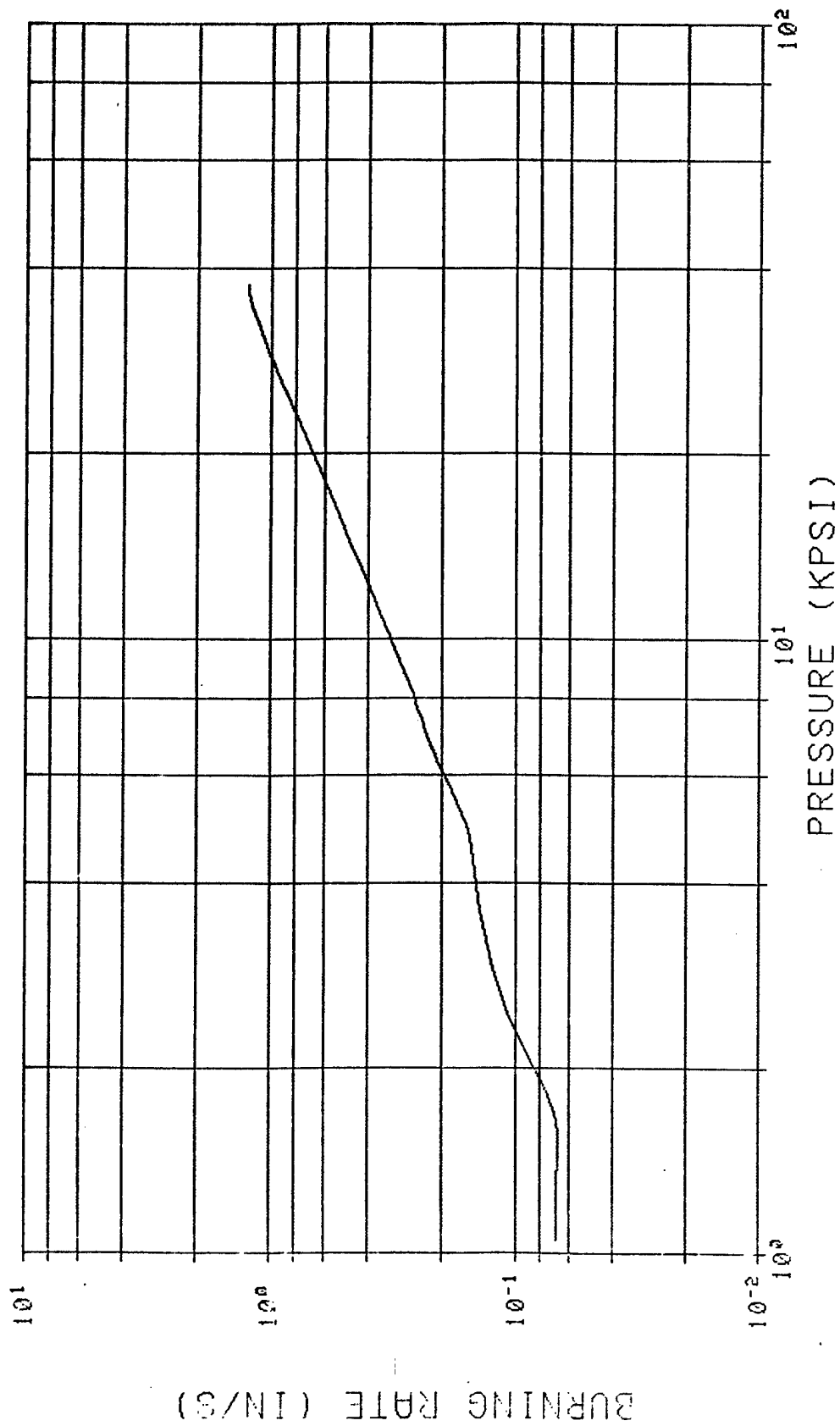


FIGURE A-1. UNCATALYZED PROPELLANT CLOSED BOMB RESULTS

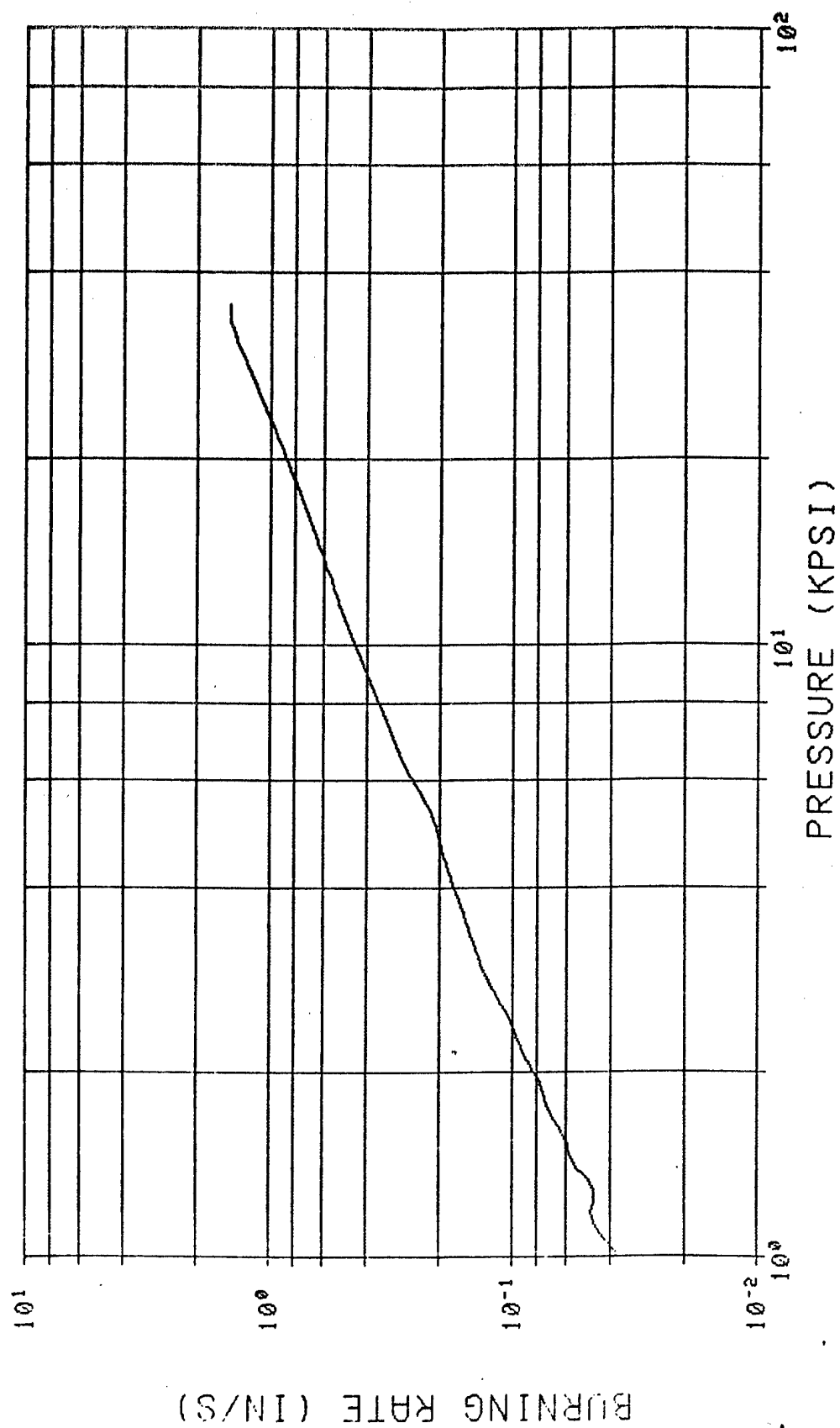


FIGURE A-2. CATALYZED PROPELLANT CLOSED BOMB RESULTS

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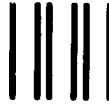
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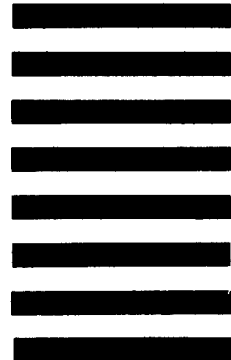


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